allyl radicals, the π-bond order of atom 2 must be four times the p_{12} of the allyl radical.[10] Thus N_2 for propargylene is found to be

$$N_2 = 2 + 4(\sqrt{2}/2) = 4.828 \quad (2)$$

This value is considerably larger than the bond order of the central atom of trimethylenemethane.[10a] This observation prompted further exploration of this point to see what the trend would be in the higher homologs. The N_2 and $N_{(N+1)/2}$ were calculated[11] for the homologous series $C_{2n+1}H_2$, of which propargylene is the first member. The results of the calculation of the mobile bond order of the central atom and the second atom of this series are shown in Table I. It will be noted that the maximum bonding appears at the second atom of the chain and that it gradually drops off with increasing chain length. Bonding at the central carbon varies with values considerably less than trimethylenemethane with the exception of propargylene, in which case the central carbon and the second carbon atoms are identical.

TABLE I
MAXIMUM BOND ORDER

$2n + 1$	Middle atom	Second atom
3	4.82842702	4.82842702
5	4.30940092	4.73205078
7	4.61312556	4.72077644
9	4.46124646	4.71802250
11	4.57580119	4.71708256
13	4.50359154	4.71669075
15	4.56291401	4.71650353
17	4.52056789	4.71640506
19	4.55697888	4.71634921
21	4.52914387	4.71631563
23	4.55376321	4.71629447

F_1 for II is 1.318 while F_2 for I is only 1.155. Both of these are greater than the 1.04 for the benzyl radical but less than the 1.73 for the methyl radical.[14] Caution should, however, be exercised since HMO theory does not recognize differences in multiplicity. Therefore the value of F_1 for II does not depend upon whether we consider a singlet or a triplet propargylene. Since singlet–triplet inversions are forbidden, the singlet and the triplet are two different species which should react differently with respect to "...neutral nonpolar reagents, such as free radicals...."[15] The calculations do not show any difference in the F_1 between singlets and triplets.

The F_2 for propargylene is greater by 0.096 bond order unit than for atom 1 of I. The literature accepts 4.732 as the maximum possible bond order. This was chosen so that all F_i would be positive. It should be noted from this definition that F_2 for II is -0.096. However, in order to avoid confusion in the future as to what value of $N_{\max}$ is being used, perhaps it might be best to accept 4.732 as a standard reference point. This would serve index of free valence much as TMS serves nmr. In both instances species exist on both sides of the reference.[16]

Registry No.—Trimethylenemethane, 10316-06-0; propargylene, 2008-19-7.

Acknowledgment.—The author wishes to thank Dr. W. M. Jones for the helpful suggestions and discussions which he has offered during the writing of this paper.

[10] C. A. Coulson and A. Streitwieser, "Dictionary of π-Electron Calculations," W. H. Freeman and Co., San Francisco, Calif., 1965, p 183.

[10a] NOTE ADDED IN PROOF.—After submission of our paper it was discovered that the same conclusions were reached by W. M. A. Smit and D. H. N. den Boer, *Theoret. Chim. Acta*, **6**, 358 (1966).

[11] N_r was calculated by computer[12] using the following equations:[13]

$$C_{ir} = \frac{\sqrt{2}}{n+1} \sin \frac{i\pi}{n+1} r$$

$$P_{rs} = \sum_j N_j C_{jr} C_{js}$$

where r and s are neighbors, and

$$N_r = \sum P_{rs}$$

over all neighbors s.

[12] We wish to express our thanks to the University of Florida Computing Center for the use of its computer.

[13] A. Streitwieser, Jr., ref 5d, pp 50, 55.

[14] J. D. Roberts, ref 5a, p 58.

[15] J. D. Roberts, ref 5a, p 57.

[16] A referee has suggested doing away with F_i completely and using instead N_r as a stability index. This would have the advantage of not having to worry about maxima.

1,2- and 1,4-Addition Products from the Reaction of Benzylmagnesium Chloride and *trans*-α-Phenylchalcone

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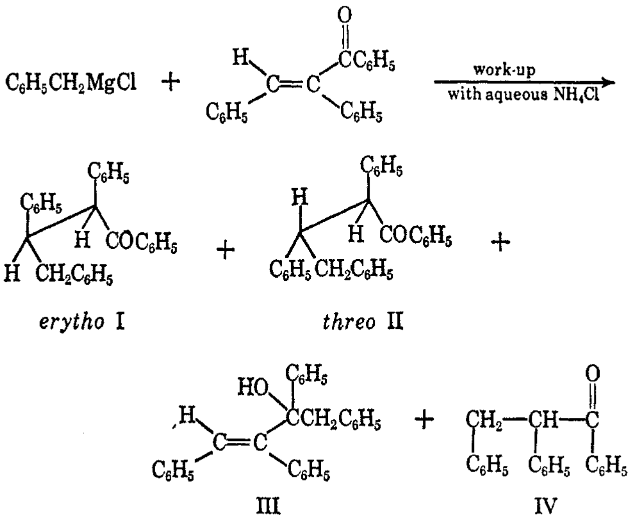
In the hope of photochemically synthesizing 1,2,3,4-tetraphenylcyclobutanol we have had occasion to synthesize the stereoisomers of 1,2,3,4-tetraphenylbutanone (Scheme I). Bergmann, Winter, and Schreiber[1] originally reported that the reaction of *trans*-α-phenylchalcone with benzylmagnesium chloride results in the formation of only one 1,4-addition diastereoisomer in 26% yield having a melting point of 178–179°. No 1,2-addition product was reported. When

SCHEME I



[1] E. Bergmann, D. Winter, and W. Schreiber, *Ann.*, **500**, 122 (1933).

this compound was treated with acetyl chloride, a substance, mp 197–198°, having the same composition as the starting material was recovered, and the higher melting material was said to be the second diastereoisomer.

This reaction was repeated and worked up using the saturated ammonium chloride method. From ethereal solution there first crystallized an isomer of 1,2,3,4-tetraphenylbutanone, in 38% yield, having mp 197–198°. Further concentration of the mother liquor yielded the second diastereoisomer (16%), mp 128–129°. Treatment of the 128–129° melting compound with acetyl chloride caused no change. We can only conclude that the 178–179° melting compound reported earlier[1] was an impure form of the 197–198° melting compound and that the former was simply purified in the course of the acetyl chloride treatment. These results are in accord with the observation by Crawford[2] that treatment of an ester of 2,3,4-triphenylbutyric acid with phenyllithium resulted in the formation of two 1,2,3,4-tetraphenylbutanones, one melting 198–199° and the more soluble melting at 125–126°.

Continued fractional crystallization of the mother liquors yielded two more compounds. 1,2,3-triphenylpropanone (IV) was obtained in 1% yield and finally, in 2% yield, the 1,2-addition product, 1,2,3,4-tetraphenyl-3-buten-2-ol. Some earlier publications[1,3] have indicated that only 1,4-addition products were isolated from α-phenylchalcone and various Grignard reagents. We are not certain of the origin of the 1,2,3-triphenylpropanone.

The higher melting and less soluble isomer of 1,2,3,4-tetraphenylbutanone has been tentatively assigned the *erythro* configuration. If one examines the two diastereoisomers in what one would predict to be their most stable conformations, it may be seen that the *erythro* compound "comes closer" to having a center of symmetry than does the *threo* compound. In the case of 1,2,3,4-tetraphenylbutane[4] as well as 2,3-diphenylbutane,[5] the more symmetrical *meso* form has been identified as the higher melting isomer.

Experimental Section[6]

trans-α-Phenylchalcone was synthesized, according to the method of Dornow and Boberg[7] condensing benzaldehyde and desoxybenzoin in refluxing benzene with piperidine catalyst. The yield of product, melting at 102.5–104.0°, was 86% (lit.[8] mp 103–103.5°). Benzylmagnesium chloride was made according to the method of Gilman[9] and was used immediately.

Reaction of Benzylmagnesium Chloride with *trans*-α-Phenylchalcone.—To 1500 ml of an ethereal solution of 43.7 g (0.15 mole) of *trans*-α-phenylchalcone, 400 ml of an ethereal solution of benzylmagnesium chloride [prepared from 4.9 g (0.20 g-atom) of magnesium and 26.0 g (0.21 mole) of benzyl chloride] was added over a 30-min period. The reaction was carried out under nitrogen. After standing at room temperature for 2 hr, the mixture was hydrolyzed with saturated aqueous ammonium chloride. The ether layer was decanted and, after standing in the refrigerator, deposited a white solid; a smaller amount of the same solid was obtained from acetone rinsings of the glassware and the inorganic residue. The total, after recrystallization from acetone, was 21.9 g (38%) of *erythro*-1,2,3,4-tetraphenylbutanone: mp 197–198°; nuclear magnetic resonance (nmr) spectra (numbers in parentheses indicate integrated intensity) τ 2.0–3.3 (20), τ 4.85 doublet (0.8), τ 6.10 multiplet (0.9), and τ 7.25 multiplet (1.7).

The mother liquor was removed under vacuum at room temperature. The yellow solid which remained was twice recrystallized from methanol yielding 9.0 g (16%) of *threo*-1,2,3,4-tetraphenylbutanone: mp 128–129°; nmr spectra τ 2.0–3.3 (20), τ 5.12 doublet (0.9), τ 6.15 multiplet (0.8), and τ 7.10 multiplet (2.0).

The methanolic mother liquor was further concentrated and yielded two additional fractions, the first of which consisted of 0.50 g (1%) of a crystalline solid, mp 143.5–144.0°, analyzing for $C_{21}H_{20}O_2$. When this substance was treated with acetyl chloride in benzene under reflux it was quantitatively converted to 1,2,3-triphenylpropanone, mp 120–121°. The compound $C_{21}H_{20}O_2$ appears to be a hydrate of 1,2,3-triphenylpropanone. A mixture melting point with an authentic sample was not depressed (see below).

The second fraction from the methanolic mother liquor 1.0 g (2%) was 1,2,3,4-tetraphenyl-3-buten-2-ol: mp 144.5–146°; nmr spectra τ 2.3–3.3 (21) (vinylic proton not resolved from phenyls), τ 6.50 (2.0), and τ 7.86 (0.9).

Anal. Calcd for $C_{28}H_{24}O$: C, 89.32; H, 6.43. Found: C, 89.59; H, 6.72.

Preparation of 1,2,3-Triphenylpropanone.—This compound was prepared according to the method of Cragoe and Pietruszkiewicz[10] by treating 9.5 g (0.075 mole) of benzyl chloride with 9.8 g (0.050 mole) of desoxybenzoin in the presence of 4.4 g (0.11 mole) of sodium hydroxide suspended in 50 ml of toluene. The mixture was heated on a steam bath and yielded 10.5 g (73%) of 1,2,3-triphenylpropanone, mp 120–121° (lit.[11] mp 121°).

Registry No.—I, 10126-56-4; II, 10126-57-5; III, 10126-58-6; IV, 4842-45-9; benzylmagnesium chloride, 6921-34-2; *trans*-α-phenylchalcone, 7512-67-6.

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[5] F. D. Greene, *J. Am. Chem. Soc.*, **77**, 4869 (1955).

[6] Melting points are uncorrected. Nmr spectra were determined with a Varian A-60 instrument using tetramethylsilane as internal standard. Elemental analyses were performed by Micro-Tech Laboratories of Skokie, Ill. Known compounds gave correct C and H analyses.

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[10] O. Cragoe and O. Pietruszkiewicz, *J. Org. Chem.*, **22**, 1338 (1957).

[11] O. Fiesselman, *et al.*, *Chem. Ber.*, **89**, 30 (1956).

Polylithiated Species from 1-Phenylpropyne and Organolithium Reagents[1]

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It has previously been shown that primary organolithium compounds react with diphenylacetylene to give a dilithium compound whereas under some conditions *t*-butyllithium gives products arising from electron transfer.[2]

This report is prompted by the recent observation by West, Carney, and Mineo[3] that terminal alkynes re-

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[1] Research sponsored by AFOSR(SRC)-OAR, U. S. Air Force Grant No. 720-65.

[2] J. E. Mulvaney, Z. G. Gardlund, and S. L. Gardlund, *J. Am. Chem. Soc.*, **85**, 3897 (1963); J. E. Mulvaney, Z. G. Gardlund, S. L. Gardlund, and D. J. Newton, *ibid.*, **88**, 476 (1966).

[3] R. West, P. A. Carney, and I. C. Mineo, *ibid.*, **87**, 3788 (1965). See also K. C. Eberly and H. E. Adams, *J. Organometal. Chem.* (Amsterdam), **3**, 165 (1965).